

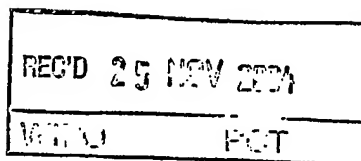
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## A TWO-STEP SYSTEM FOR IMPROVED INITIAL AND FINAL CHARACTERISTICS OF A BIOMATERIAL

The present invention relates to a system for chemically bonded ceramic (CBC) materials, preferably a dental filling material or an implant material, comprising a two-step procedure. This system includes an initial working part-system to provide for improved early-age properties and a second main system to provide for improved end-product properties including bioactivity. The invention also relates to the powdered materials and the hydration liquid, respectively, as well as the formed ceramic material.

### STATE OF THE ART AND PROBLEM

The present invention relates to binding agent systems of the hydrating cement system type, in particular cement-based systems that comprise chemically bonded ceramics in the group that consists of aluminates, silicates, phosphates, carbonates, sulphates and combinations thereof, having calcium as the major cat-ion, and in addition to the said system a second early age binding system is included. The invention has been especially developed for biomaterials for dental and orthopaedic applications, both fillers and cements as well as implants including coatings and carriers for drug delivery, but can also be used as fillers in industrial applications in electronics, micro-mechanics etc or in the construction field.

### BRIEF ACCOUNT OF THE INVENTION

This invention relates especially to the combination of improved early-age properties (properties achieved within the first ten minutes up to some hours) and the property development towards the final stage which for different properties are achieved after some days or weeks. The present invention specifically relates to the problems of initial moulding ability, initial strength, heat evolved and early colour/transmittance development as well as high strength, viscoelasticity and other mechanical properties, i.e. the problem of being able to optimise a complex property profile in a bioactive product and at the same time to optimise the property profile of a the system during processing of the same to form the product.

The chemically bonded ceramic system for dentistry based on Calcium aluminate minerals has two drawbacks related to initial strength and possible expansion. The final strength is reached after about 7 days, but the strength during the first hour is lower than that of a temporary filling material. The magnitude of the expansion may be too high

not to raise questions from the dental community. According to ISO 1559 an amalgam restorative should have a dimensional stability within  $-0.15$  to  $+0.2$  linear %. The level  $0.2$  % can be obtained in the Ca-aluminate based system, but expansion close to zero is desirable.

5

For orthopaedic applications an additional question deals with the heat evolved during the initial setting and hardening. This is more pronounced for treatments where larger amounts of biomaterial are injected.

- 10 The present invention addresses these issues. A low initial strength can cause failures during the first 24 hours and a somewhat too high expansion may cause tooth cracking in weakened teeth after the replacements of earlier fillings. The crucial question is how to increase the initial strength without affecting the final properties negatively, and is not a straightforward matter and demands a careful microstructural design. The use of
- 15 two periods with different chemistry involved as in the present invention solves the problem with initial desired features of the biomaterial and the end-product characteristics.

- 20 Accordingly, the present invention aims at providing a system for CBC materials, preferably biomaterials, having improved controllability concerning its initial viscosity and consistency as well as heat evolved upon mixing of the powdered material and the hydration liquid of the system and early-age properties (initial strength, pore closure, translucency and early obtained bioactivity) and optimal end-product properties such as mechanical properties including compressive and bending strength and a sufficiently
- 25 high E-modulus, a certain viscoelasticity and appropriate hardness, in the hydrated CBC product. This combination of improved initial properties and final properties is achieved by using optimised combination of chemically compatible systems, where the first system is working in the initial phase in combination with the main system. The over-all system works with pH-changes that are set by the selected part systems. The present
- 30 invention is related to a pH controlled combination of a rapidly formed phase, primarily controlled by cross-linking chemistry and an over-all acid-base reaction of chemically bonded ceramic type, primarily controlled by hydration chemistry. The control of pH is essential in transforming the initial acid system into a bioactive system, i.e. conditions for apatite formation. The rapid change into high pH-values reduces the
- 35 risk of metal release.

These and other objectives are attained by the system, the powdered material, the hydration liquid and the ceramic material according to the invention, as defined in the claims.

- 5 According to one aspect of the invention, the powdered material and/or the hydration liquid comprises an additive of polyacrylic acid and/or a salt thereof or other polycarboxylic acids, co-polymers thereof, or polycarboxylates (i.e. a salt or ester of a polycarboxylic acid). All these refer to the PAA-system.
- 10 The function of the poly acrylic acid or a salt (PAA) thereof can be divided into dispersing ability and cross-linking. As is understood, in the case with the cross-linking poly acid, the powdered material (the reactive glass and the calcium aluminate material) is first dissolved in the liquid, where after Ca- and Al-ions cross-links the polyacrylic acid to form a polyacrylate polymer, and other Ca- and Al-ions hydrate to
- 15 form hydrated calcium aluminate material in a second step. The resulting, hydrated material is a composite of CBC material and a cross-linked polyacrylate polymer. For an optimised formation of the two part composite – a biomer – the CBC system requires Ca-aluminate, inert glass or other inert filler and the Polyacrylic system, a glass ionomer type of cement, a poly acrylic acid and/or a salt thereof and reactive glass
- 20 including a phosphate –containing glass, the composition of which is at least as soluble as traditional bioactive glasses. The initial low pH of the system induces a dissolution of both the reactive glasses and the basic Ca-aluminate system or other chemically bonded ceramics of the same type, e.g. Ca-silicates.
- 25 Thus binding phases may work at separate time or work over-lapped in the over-all hardening process facilitating the combination of potential early-age properties with high performance end features especially related to biomechanical and biochemical properties.

30 **DETAILED DESCRIPTION OF THE INVENTION**

Relating to a survey article on medical and scientific products by L.H. Hench

“Engineered Materials Handbook” Vol 4, ASM International 1991, pp1007-1013,

(especially Figures 1 and 2 p 1008) the present invention deals with bioactive materials of an additional type, the type of which could be defined as type 5, i.e. with even faster

- 35 dissolution and precipitation of phases than in the traditional bioactive glasses and/or resorbable material .

One route according to the present invention that surprisingly yields good initial results and improved final properties is to make a hybrid material of a glass ionomer cement and minerals of calcium aluminate, maintaining a bioactive feature of the system. Glass ionomer cements consist of glass and poly acrylic acid. The acid dissolves the glass and the ions from the glass cross-link the acid and the material hardens. The reaction is rather rapid and the near final strength is reached after about one hour. By exchanging fractions of the glass for calcium aluminate and a corresponding fraction of the PAA for water (with accelerator) a hybrid material can be formed. The liquids composition are controlled via

$$\frac{w_c}{c} + \frac{PAA}{\text{reactive\_glass}} + \frac{w_{gic}}{\text{reactive\_glass}}$$

with a  $0.2 < w_c/c < 0.45$  (refers to the CBC-system),  $0 < PAA/(\text{reactive glass}) < 0.21$  and  $0.2 < w_{GIC}/(\text{reactive glass}) < 0.45$  (refers to the glass ionomer system). The PAA can be applied as a solution and/ or as solid acid component.

Since the initial pH is acidic, the PAA reaction occurs first and as the acid is cross-linked the pH increases and the hydration of the Ca-aluminates continues. The material has a much higher initial strength than that of the pure ceramic system. The final strength is higher than that of the GIC. The microstructural variables are controlled by the reactive glass, the poly acrylic acid including the pH, the Ca-aluminate and inert fillers.

The initial solution should have a pH < 7, preferably 1–4, enhancing the cross-linking of the polycarboxylic. The pH increases when the polycarboxylic system meets the CA-system, resulting in a basic over-all system at pH > 7. The amounts of the polyacrylic acids are controlled to maintain pH < 7 up to 30 minutes. After final hydration the pH approaches neutrality from the basic side. One problem with pure Glass Ionomer systems, which are based on polycarboxylic is the corrosion resistance sensitivity. The basic CAH system neutralises the initial acidity in the polyacrylic systems. The present

invention could be looked upon as a two-phase biomaterial composed of two different biomaterials where the first is activated to take care of necessary early-age phenomena and the second biomaterial to establish the property profile of the end-product, included being a bioactive material.

5

The control of pH, especially the effect of yielding  $\text{pH} > 7$  early in the process - after initial acidic condition - is essential in transforming the initial acid system into a bioactive system, i.e. conditions for apatite formation, the requirements of which is high pH and a chemical surrounding of ions including calcium, phosphate and hydroxyl ions - the phosphate ions originating from phosphate glass, body liquid or from P-containing bonding materials, the hydroxyl ions from the dissolution of the Ca-aluminate system or added bases, preferably Li-hydroxide and/or Ca-hydroxide. The high pH contributes to formation of aluminate ions ( $\text{Al}(\text{OH})_4^-$ ) in stead of aluminium ions ( $\text{Al}^{3+}$ ).

15 Reactive filler particles in the present invention are composed of reactive glass, a phosphorous-containing glass and chemically bonded ceramics, preferably Ca-aluminates, preferably  $\text{CA} = (\text{CaO})(\text{Al}_2\text{O}_3)$ ,  $\text{C}_{12}\text{A}_7 = (\text{CaO})_{12}(\text{Al}_2\text{O}_3)_7$  and  $\text{C}_3\text{A} = (\text{CaO})_3(\text{Al}_2\text{O}_3)$ . The composition of the reactive glass, especially the dissolution rate, is crucial. The glass grain size is also important and should be below 40 micron. The pure PAA gives an earlier general cross-linking reaction. Addition of a salt of the PAA is important in achieving improved viscosity at low w/c. The inert filler is essential for the general end-product microstructure. Its effect concerns a lowered expansion, increased radio-opacity and favoured mechanical properties, especially hardness and fracture toughness.

25

Concerning calcium aluminate phases it is preferable to use CA,  $\text{C}_{12}\text{A}_7$  and  $\text{C}_3\text{A}$ , which yield good initial strength. The addition of accelerator is dependant upon the selection of the Ca-aluminate phase. Low concentrations of lithium ions increase the reaction rate for CA. For  $\text{C}_{12}\text{A}_7$  and  $\text{C}_3\text{A}$  the effect of accelerator is more complex.

30

According to another aspect of the invention addition of a base is included to achieve a change of pH to a high pH > 7, more preferably pH > 10 after an initial "acidic" time period of approximately 5 minutes. This is to assure an optimised hydration speed.

- 5 According to another aspect of the invention addition of a further acid is included to keep the pH < 7 during a prolonged time of up to 30 minutes. This is to assure an optimised time for complete cross-linking of the acid.

- 10 Ways to induce such additional (delayed and then rapid) pH changes include release of acids/bases from a porous material (preferably nano/meso-pore structure or zeolite type structures). An additional way is coating of the particle surfaces to control the release/dissolution of pH changing species, especially the CBCs material, e.g Ca-aluminate phases by coating with for instance Na-glyconate.

- 15 The active acids can be introduced either as dried substance together with the inorganic cement or as liquid in the hydration liquid or as a combination of both dry an active acid raw material and a liquid solution of the active acid.

- 20 Suitably, said polycarboxylic has a molecular weight of 100 – 250,000, preferably 1000 – 100,000 and it is present in an amount of up to 30 %, preferably 1-20 % and most preferred 3-15 % by weight, calculated on the powdered material including any dry additives for dental applications. For orthopaedic applications where larger amounts of the material are required, as for the case of bone void fillers, e.g. for percutaneous vertebroplasty, where heat evolution is critical, higher amounts of said
- 25 polycarboxylic are used, amounts up to 30 %, preferably 15-30 %.

- It is preferred that the system comprises inert dental glass, as an additive in the powdered material, preferably at a content of 5-40 weight-% more preferred 15-35 %. The particle size is critical in establishing high homogeneity. It is preferred that the
- 30 particle size is 0.1-5  $\mu\text{m}$ , more preferable 0.2 – 2  $\mu\text{m}$ , and most preferable 0.3-0.7  $\mu\text{m}$ . The dental glass may contain low amounts of less stable glass or reactive glass, preferable below 10 % of the glass content. These glasses can preferably contain fluorine and phosphor to yield fluoride ions, which contribute to F-apatite formation. According to the present invention the translucency is achieved earlier than in a pure
- 35 Ca-aluminate based system due to early pore closure.

According to one aspect of the invention the inert filler particles are composed of pre-hydrated chemically bonded ceramics of the same composition as the main binding phase. This improves the homogeneity of the microstructure and enhances the binding between reacting chemically bonded ceramics and the filler material.

According to another aspect of the present invention an additional system can be included to improve the closure of pores initially, namely by introducing a system that works independently of the pH, e.g. the semihydrate of  $\text{CaSO}_4$ , gypsum. And a further system to solidify the total system initially, the combination of phosphoric acid and zinc oxide-forming Zn-phosphate. These phases will not contribute to the long-term properties but will enhance the initial pore closure and initial strength.

The system and material according to the invention have the advantages compared to systems/materials such as glass ionomer cements and pure Ca-aluminate based systems or monomer based filling materials, that it maintains its bioactivity, that it has improved initial strength and that it has long time stability regarding both dimensional aspects, strength and minimised deterioration. The viscosity of the material can be controlled within wide frames, upon initial mixing of the powdered material and the hydration liquid, from moist granules to an injectable slurry. The material is unique in that it solidifies in at least two steps, i.e. by cross-linking of the polycarboxylic or salt thereof and by hydration of one or more systems.

#### EXAMPLE 1

Tests were performed to investigate the influence of amount of poly acid and the composition of the chemical bonded ceramic on the mechanical properties. The values are compared to commercial glass ionomer cement and amalgam.

#### Description of raw materials

Calcium aluminate ( $(\text{CaO})_3(\text{Al}_2\text{O}_3)$ ;  $(\text{CaO})(\text{Al}_2\text{O}_3)$ ,  $(\text{CaO})_{12}(\text{Al}_2\text{O}_3)_7$ ), dental glass filler (Schott), poly acid (PAA = poly acrylic acid  $\text{Mw}=50,000$ , Na-PAMA = poly(acrylic-co-maleic acid) sodium salt  $\text{Mw}=50,000$ ) and reactive glass. Glass ionomer cement (Fuji II, GC-corp) and Amalgam (Dispersalloy, Dentsply).



### Description of materials

Calcium aluminate was mixed with dental glass, reactive glass, poly acrylic acid and poly(acrylic-co-maleic acid) sodium salt. The calcium aluminate phases were synthesised via a sintering process where first CaO and Al<sub>2</sub>O<sub>3</sub> was mixed to the desired composition and then sintered at elevated temperature for 6 hours. The formed calcium aluminate lumps were crushed and jet-milled to a mean grain size of 1.5 µm and a maximum grain size of 9 µm. The dental glass, calcium aluminate and poly acids were mixed with acetone and Si<sub>3</sub>N<sub>4</sub> marbles for 14 hours to obtain the desired homogeneity. Formulations were made according to (in wt.%):

10

Formulation	Calcium aluminate phase	Inert glass	Reactive glass	Na-PAMA Mw 5000	PAA Mw 50000
1	(CaO)(Al <sub>2</sub> O <sub>3</sub> ) 63.5	33.5	-	3	-
2	(CaO)(Al <sub>2</sub> O <sub>3</sub> ) 47	25	20	3	5
3	(CaO)(Al <sub>2</sub> O <sub>3</sub> ) 31	17	40	2	10
4	(CaO)(Al <sub>2</sub> O <sub>3</sub> ) 13	6	60	1	20
5	(CaO)(Al <sub>2</sub> O <sub>3</sub> ) / (CaO) <sub>12</sub> (Al <sub>2</sub> O <sub>3</sub> ) <sub>7</sub> mineral mixture of 90/10 and 47 in total	25	20	3	5
6	(CaO)(Al <sub>2</sub> O <sub>3</sub> ) / (CaO) <sub>12</sub> (Al <sub>2</sub> O <sub>3</sub> ) <sub>7</sub> mineral mixture of 50/50 and 31 in total	17	40	2	10

The formulations were placed in 5 ml jars and wet with liquid and blended in a "rotmix" (3M ESPE) for 15 seconds followed by centrifugation for 3 seconds. In addition 18mM of LiCl was added to further increase the hydration speed. The liquids composition were controlled via

15

$$\frac{w_c}{c} + \frac{PAA}{\text{reactive\_glass}} + \frac{w_{GIC}}{\text{reactiv\_glass}}$$

with a  $w/c=0.32$  (refers to the CBC-system),  $PAA/(\text{reactive glass})=0.14$  and  $w/(\text{reactive glass})=0.37$  (refers to the glass ionomer system).

20

### Description of tests

- The diametral tensile strength was measured for the six formulations, the amalgam and the glass ionomer cement. The strength was measured after 15 min, 60 min, 4 hours and 24 hours. All samples were stored in phosphate buffer solution (pH 7.4) before measurement of DTS. The pH was measured by soaking a defined amount of material in distilled water (material/water 1/3 by volume) for the same time periods as the DTS-measurements. All storage were at 37 degrees C.

### Results

The results of the tests were:

Material	15 min (MPa) / pH	60 min (MPa) / pH	4 hours (MPa) / pH	24 hours (MPa) / pH
Formulation 1	1.5 / 8	6.2 / 10	8.3 / 11	20.1 / 11.1
Formulation 2	2.1 / 3.2	8.5 / 6	11.1 / 8	26.8 / 10.9
Formulation 3	4.3 / 3	9.1 / 5.7	14.7 / 7.3	26.7 / 10.5
Formulation 4	8.2 / 2.4	10.4 / 4.2	12.2 / 6.3	14 / 7
Formulation 5	3.1 / 3	8.7 / 6.6	12.4 / 9	29 / 11.3
Formulation 6	5.5 / 2.1	10.3 / 5.7	15.4 / 7.6	27.7 / 10.9
Fuji II	10.1 / 2	12.3 / 2.5	11.2 / 3.1	11.1 / 4
Dispersalloy	2.1 / n.a.	9.1 / n.a.	14.2 / n.a.	29.3 / n.a.

10

- By adding PAA and reactive glass to the calcium aluminate system an increased initial strength can be achieved. Also, by adding  $(\text{CaO})_{12}(\text{Al}_2\text{O}_3)_7$  the reaction speed is increased and thus also the initial strength. The increase in pH over time for the formulations with calcium aluminate shows that the hydration reaction is similar to the pure calcium aluminate system.

15

### EXAMPLE 2

- A series of tests were performed to investigate the influence of poly acid on the acid erosion resistance. The values are compared to commercial glass ionomer cement (Fuji II) and to commercial calcium aluminate based dental material (DoxaDent, Doxa AB).

20

### Description of raw materials

Calcium aluminate  $(\text{CaO})(\text{Al}_2\text{O}_3)$ , dental glass filler (Schott), Na-PAMA = poly(acrylic-co-maleic acid) sodium salt, poly acrylic acid Mw 50000, reactive glass.

### Description of tests

Test a) to c) investigated:

- a) the acid erosion of Fuji II
- 5 b) the acid erosion of DoxaDent
- c) as formulation 3 described in Example 1.

The calcium aluminate phases were synthesised via a sintering process where first CaO and Al<sub>2</sub>O<sub>3</sub> was mixed to the desired composition and then sintered at elevated  
10 temperature for 6 hours. The formed calcium aluminate lumps were crushed and jet-milled to a mean grain size of 3 µm and a maximum grain size of 9 µm. The dental glass, reactive glass, calcium aluminate and poly acids were mixed with acetone and Si<sub>3</sub>N<sub>4</sub> marbles for 14 hours to obtain the desired homogeneity. The samples in test c) where blended to the desired water to cement ratio in 5 ml jars and rotated at 500 rpm  
15 for 15 seconds. DoxaDent and Fuji II samples were made according to the manufactures instructions. The acid erosion was measured according to ISO-9917.

The results showed that the tests in b and c exhibited an acid erosion of below 0.01 mm/h whereas the glass ionomer cement showed a acid erosion of 0.1 mm/h. Thus the  
20 results show that addition of poly acid to calcium aluminate does not reduce its acid resistance.

### **EXAMPLE 3**

A series of tests were performed to investigate the possible in-vitro bioactivity of the  
25 calcium aluminate material, the glass ionomer cement and the combination of the two. Bioactivity is often defined as the ability to form apatite on the surface in contact with body fluids.

### Description of materials

30 Calcium aluminate was mixed with dental glass, reactive glass, poly acrylic acid and poly(acrylic-co-maleic acid) sodium salt. The calcium aluminate phases were synthesised via a sintering process where first CaO and Al<sub>2</sub>O<sub>3</sub> was mixed to the desired

composition and then sintered at elevated temperature for 6 hours. The formed calcium aluminate lumps were crushed and jet-milled to a mean grain size of 2.5  $\mu\text{m}$  and a maximum grain size of 9  $\mu\text{m}$ . The dental glass, calcium aluminate and poly acids were mixed with acetone and  $\text{Si}_3\text{N}_4$  marbles for 14 hours to obtain the desired homogeneity.

- 5 Formulations were made according to (in wt.%):

Formulation	Calcium aluminate phase	Inert glass	Reactive glass	Na-PAMA Mw 5000	PAA Mw 50000
1	$(\text{CaO})(\text{Al}_2\text{O}_3)$ 63.5	33.5	-	3	-
2	$(\text{CaO})(\text{Al}_2\text{O}_3)$ 47	25	20	3	5
3	$(\text{CaO})(\text{Al}_2\text{O}_3)$ 31	17	40	2	10
4	$(\text{CaO})(\text{Al}_2\text{O}_3)$ 13	6	60	1	20
5	$(\text{CaO})(\text{Al}_2\text{O}_3)$ / $(\text{CaO})_{12}(\text{Al}_2\text{O}_3)_7$ mineral mixture of 90/10 and 47 in total	25	20	3	5
6	$(\text{CaO})(\text{Al}_2\text{O}_3)$ / $(\text{CaO})_{12}(\text{Al}_2\text{O}_3)_7$ mineral mixture of 50/50 and 31 in total	17	40	2	10

- 0.5 grams of each the formulation were placed in 5 ml jars and wet with liquid and blended in a mixer by 3M/ESPE for 15 seconds followed by centrifugation for 3 seconds. In addition 18mM of LiCl was added to further increase the hydration speed. The liquids composition were controlled via

$$\frac{w_c}{c} + \frac{PAA}{\text{reactive\_glass}} + \frac{w_{\text{alc}}}{\text{reactiv\_glass}}$$

- with a  $w/c=0.32$  (refers to the CBC-system),  $PAA/(\text{reactive glass})=0.14$  and  $w/(\text{reactive glass})=0.37$  (refers to the glass ionomer system). For comparison samples of GIC were also made.

#### Description of tests

- The bioactivity was studied by soaking a defined amount of material in simulated body fluid (SBF) (material/SBF 1/3 by volume) for time periods of 1 day, 7 days and 21 days at 37 degrees C. After storage the samples were removed from the SBF, rinsed in distilled water and dried at 37 degrees C for 48 hours. The surface composition of the

formulations was studied with thin film X-ray diffraction ( $1^\circ$  angle) and SEM combined with EDX. For each formulation and time period 5 samples were analysed. For SEM the presence of Ca and P on the surface with a ratio 1.67 indicates formation of apatite. In XRD the peaks according to the powder diffraction file for apatite must comply with the pattern from the sample

### Results

The results from the analysis can be seen in the Table below. All formulations with calcium aluminate formed apatite on the surface after 21 days. The formulations with low amounts of calcium aluminate did not form the apatite layer as quick as the formulations with much calcium aluminate, which all had apatite on the surface after 1 day. The GIC material did not form apatite on the surface. Thus the combined material can be judged as bioactive.

Table. Results from the bioactivity tests.

<i>Material</i>	<i>1 day</i>	<i>7 days</i>	<i>21 days</i>
	<i>XRD / SEM</i>	<i>XRD / SEM</i>	<i>XRD / SEM</i>
Formulation 1	Apatite	Apatite	Apatite
Formulation 2	Apatite	Apatite	Apatite
Formulation 3	Apatite	Apatite	Apatite
Formulation 4	-	-	Apatite
Formulation 5	Apatite	Apatite	Apatite
Formulation 6	Apatite	Apatite	Apatite
Fuji II	-	-	-

The invention is not limited to the embodiments described, but can be varied within the scope of the claims.

## CLAIMS

1. A system for a chemically bonded ceramic material according to claim 1 in SE  
 5 0302844-6, characterised in that the system also comprises a reactive  
 glass and a second portion of aqueous hydration liquid ( $w_{GIC}$ ), where

$$\frac{w_c}{c} + \frac{\text{second binder phase}}{\text{reactive glass}} + \frac{w_{GIC}}{\text{reactive glass}}$$

- 10 with  $0.2 < w/c < 0.45$ ,  $0 < (\text{second binder phase})/(\text{reactive glass}) < 0.21$  and  $0.2 < w_{GIC}/(\text{reactive glass}) < 0.45$ .

2. A system according to claim 1, characterised in that it is adapted to enable  
 an initial pH to be kept  $< 7$ , more preferably  $< 4$  and most preferably 1-3 to  
 15 control properties related to different initiation time for setting and hardening of  
 the part systems.

3. A system according to any one of claims 1-2, characterised in that the  
 second binder phase comprises a polycarboxylic acid and/or a copolymer or a  
 20 salt or an ester thereof yielding the system a pH  $< 7$ , preferably  $< 4$  for the first  
 20 minutes after mixing, preferably, a pH in the interval 1-4 for the first 10  
 minutes, and most preferably for the first 5 minutes.

4. A system according to any one of claims 1-2, characterised in that a base  
 25 is comprised in the system, so as to achieve a change of pH to pH  $> 7$ , more  
 preferably pH  $> 10$ , after an initial time period after mixing of the system of a  
 few up to approximately 5 minutes at pH  $< 7$ .

5. A system according to any one of claims 1-3, characterised in that an  
 30 additional acid is comprised in the system, so as to keep the pH  $< 7$  during a  
 prolonged time of up to 30 minutes, preferably up to 20 minutes.

6. A system according to claim 4 or 5, characterised in that the system  
 35 comprises a porous material, preferably a nano/meso-pore structure or a zeolite  
 type structure, that is able to release said base or acid, respectively.

7. A system according to claim 4 or 5, characterised in that particles of said first binder phase are coated with a dissolution-reducing layer, preferably comprising a glyconate.
- 5 8. A system according to any one of the preceding claims, characterised in that it comprises inert filler particles composed of pre-hydrated chemically bonded ceramics, preferably of the same composition as said first binder phase.
9. A system according to any one of the preceding claims, characterised in  
10 that it comprises semihydrate of  $\text{CaSO}_4$  and/or a combination of phosphoric acid and zinc oxide-forming Zn-phosphate.
10. A system according to any one of the preceding claims, characterised in  
15 that the system yields an initial strength above 5 MPA measured by diametral tensile strength after 15 minutes.
11. A powdered material according to claim 7 in SE 0302844-6, characterised  
in that for dental applications, said polycarboxylic acid or copolymer or salt or  
20 ester thereof has a molecular weight of 100 – 250,000, preferably 1000 – 100,000 and it is present in an amount of up to 30 %, preferably 1-20 % and most preferred 3-15 % by weight, calculated on the powdered material including any dry additives.
12. A powdered material according to claim 7 in SE 0302844-6, characterised  
25 in that for orthopaedic applications, said polycarboxylic acid or copolymer or salt or ester thereof has a molecular weight of 100 – 250,000, preferably 1000 – 100,000 and that it is present in an amount of up to 30 %, preferably 5-25 % and most preferred 10-15 % by weight, calculated on the powdered material  
30 including any dry additives.

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